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THE INFLUENCE OF ELECTRODE REACTION KINETICS  
ON THE POLARIZATION OF FLOODED POROUS ELECTRODES

by

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Abstract

UNPUBLISHED PRELIMINARY DATA

In calculation of the polarization curves for flooded porous electrodes, the nature and parameters of the electrode kinetic expression used in the mathematical model profoundly influence the results of the computation. Using a recently developed numerical technique for performing such calculations, the effects of parameter values in a Volmer type kinetic expression and of use of linear and Tafel approximations to this expression are examined. The calculational procedure avoids assumptions of uniformity of electrolyte composition and conductivity and, by comparison with earlier methods involving these restrictions, permits evaluation of the influence of such assumptions on calculated electrode overpotentials. The results of this investigation illustrate the difficulty in attempting to simply relate porous electrode polarization to that of an equivalent plane surface and the necessity of analyzing each case of interest.

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The polarization behavior for a porous electrode differs considerably from that characterizing the same electrode reaction conducted at a plane surface. The distribution of the reaction over the extended active surface in the electrode and the transport of current or reacting species to reaction sites within the porous body are important factors in establishing the overpotential-current density relationships for such systems. Although limited in effectiveness by the transport restrictions, the increased surface permits the porous electrode to operate at overpotentials significantly lower than those occurring at a solid electrode at the same superficial current densities. This characteristic is one of the important advantages of porous electrodes in electrochemical energy conversion devices.

Polarization of flooded porous electrodes has been considered by several investigators [1-9], usually under the assumption of some simple form for the local electrode kinetic expression. Under quite restrictive additional assumptions, frequently those of uniform electrolyte concentration or potential in the pores, explicit porous electrode overpotential expressions have been derived; unfortunately the conditions assumed are often not applicable. In order to examine the polarization behavior of a much broader class of electrodes and to determine the effect of the most commonly invoked simplifying assumptions upon predictions of electrode

overpotential, recently developed numerical techniques for analysis of flooded porous electrodes<sup>10</sup> were employed in the present investigation. In this way the dependence of the overall porous electrode polarization curve on the nature and parameters of the electrode kinetic expression were determined without invoking assumptions of uniform concentration, conductivity, or potential of the electrolyte in the pores. It is found that the assumptions of some of the more simplified treatments may strongly influence the polarization behavior predicted.

### Scope

This study is concerned with flooded porous electrodes, that is, those with no gas phase present in the pores, and especially with electrodes in which no bulk flow of electrolyte occurs in the pores. Here polarization signifies the effective overpotential of the electrode; that which would be observed at the face of the porous matrix (thus excluding ohmic potential drop and any mass transfer effects in the bulk electrolyte). The effects of any changes in the electrode matrix, or in the character of the reaction sites, during the operation of the electrode are not considered. Further, the treatment is directed towards electrodes whose geometry can be approximated by plane slabs, either symmetrically exposed to the electrolyte and counter-electrode on two sides or sealed on one side. An electrode matrix with conductivity sufficiently high as to be isopotential has been assumed.

### The One Dimensional Porous Electrode

The complex structure of a porous electrode is almost always reduced for purposes of analysis to a one dimensional representation. Then the entire system is treated as a homogeneous macroscopic region of electrolyte with a distributed current (and reacting species) source which represents the reaction occurring at the electrode-electrolyte interfaces. This investigation is based on such a model. The approach amounts to averaging over the microscopic complexities of the pore network and is valid so long as the characteristic dimensions of this fine structure are small compared to distances over which there is significant variation in concentration or potential.

### Previous Work

Although there exist a number of published analyses of the behavior of flooded, non-flow, porous electrodes, all in essence based on the one dimensional model, there are not many essentially different methods presented for predicting polarization curves. These techniques can be grouped according to the simplifying assumptions made concerning the state of the electrolyte in the pores and according to the type of kinetic expression used. They are well represented by a few examples.

In 1956 Ksenzhek and Stender<sup>1</sup> developed an expression for the polarization of an infinitely thick porous electrode in which the electrolyte concentration was assumed

uniform in the pores. A hyperbolic sine type electrode kinetic expression was used (Volmer type without concentration overpotential). This predicted polarizations considerably less than for the equivalent flat plate but eventually, at very high current densities, increasing twice as rapidly with increasing logarithm of superficial current density.

Euler and Nonnenmacher<sup>3</sup> treated the case of uniform electrolyte composition in an electrode of finite thickness using a linear (equivalent conductivity) kinetic expression. For the condition of high matrix conductivity this yielded a linear polarization curve with a slope considerably less than that for the corresponding plane surface. Newman and Tobias<sup>4</sup> used a Tafel type kinetic expression under similar assumptions. The resulting polarization predictions, for high electrode conductivity, approached those of Ksenzhek and Stender at high current densities.

Ksenzhek<sup>5</sup> later considered the polarization of infinitely thick porous electrodes in which the conductivity of the pore electrolyte was so high that the local electrode potential was constant throughout the system. The problem then reduced to that of a heterogeneous chemical reaction occurring in a porous body with the overpotential serving as a reaction parameter. A local kinetic expression of the Tafel type was employed. This treatment yielded a polarization curve for the

electrode with twice the Tafel slope of the equivalent plane surface but with lower overpotentials over most practical current density ranges. The same author, in another article<sup>6</sup>, also examined thin porous electrodes but here assumed uniform electrolyte concentration in the pores.

Austin<sup>8</sup> examined electrodes of finite thickness with reactions characterized by Volmer kinetics both under the conditions of constant overpotential along the pore and under that of uniform reactant concentration. In the first case, solutions were derived for reactions of low exchange current density; in the second, solutions were restricted to conditions of high overpotential where the Tafel approximation to kinetic expression could be used. He also sought to develop a porous electrode polarization expression for Tafel kinetics where neither potential nor reactant concentration was uniform in the pores, but the resulting expression involved the overpotential both at the face and center of symmetry of the electrode, the latter not an independent parameter of the system.

Recently Gurevich and Bagotsky<sup>9</sup> have presented a detailed analysis of steady state operation of flooded porous electrodes of definite thickness where reactants and products are electrically neutral substances (non ionic). Volmer kinetics were used and variations in reactant and product concentrations and overpotential

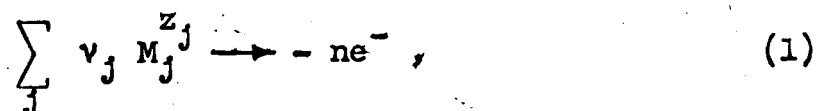
considered. Explicit general solutions were not derived but limiting current density-electrode overpotential expressions were presented for conditions of low and high polarizations.

In investigating how precisely the current distribution in a porous electrode can be determined, Euler and Müller<sup>11</sup> discussed the influence of the form of the reaction kinetic expression but restricted consideration to the linear and Tafel forms under the assumption of uniform electrolyte composition in the pores.

#### Determination of Porous Electrode Polarization Curves

The method of prediction of flooded porous electrode polarization curves utilized in this investigation is based upon the mathematical description of transport of the species present in the pore electrolyte. As these species constitute both reaction participants (together perhaps with components of the matrix) and the carriers of current in the electrolyte, such treatment avoids assumptions as to uniformity of concentration, conductivity or potential in the pores.

The electrode reaction occurring at the electrolyte-matrix interface can be represented by



where  $M_j$  symbolizes a reacting species of charge  $z_j$ ,

The relationship between the rate of this reaction at a

point on a pore wall and the conditions existing at that point is the electrode kinetic expression

$$i^S = f(\eta, c_j), \quad (2)$$

where the overpotential  $\eta$  is the difference between the potential,  $\phi$ , in the electrolyte and that which would exist at equilibrium (at bulk concentrations); the reacting species concentrations are  $c_j$ ; and the transfer current density,  $i^S$ , is used as a measure of rate. Potentials are conveniently expressed with reference to the uniform potential of the matrix.

For the one dimensional model previously described, the flux  $N_j$  of any species  $j$  is given, in the absence of electrolyte flow in the pores, by

$$N_j = -D_j \frac{dc_j}{dy} - z_j e u_j c_j \frac{d\phi}{dy}, \quad j=1, \dots, m \quad (3)$$

where the terms on the right hand side represent respectively diffusion under a concentration gradient and migration of charged species under a potential gradient. The electric current density in the electrolyte,  $i$ , is carried by the charged species and may be related to their fluxes

$$i = F \sum_j^m z_j N_j. \quad (4)$$

At steady state the conservation of any species requires that

$$\frac{dN_j}{dy} = S_j \quad (5)$$

where  $S_j$  is a source term for species  $j$ . This source



represents the production (depletion) of the species in the electrode reaction at the electrode-electrolyte interfaces (which have, so to speak, vanished in the one dimensional model) and can be related to the reaction rate or, more appropriately, transfer current density for the reaction

$$S_j = \frac{av_j}{nF} i^s, \quad (6)$$

where  $a$  is the specific surface of the pore structure. Thus a set of continuity equations, one for each species present in the electrolyte, is available.

$$D_j \frac{d^2 c_j}{dy^2} + z_j \epsilon u_j \frac{d}{dy} \left( c_j \frac{d\phi}{dy} \right) + \frac{av_j}{nF} f(\eta, c_j) = 0; \quad j=1, \dots, m \quad (7)$$

These equations, taken together with the electroneutrality condition,

$$\sum_j^m z_j c_j = 0, \quad (8)$$

and appropriate boundary conditions,

$$\begin{aligned} \text{at } y = 0; \quad c_j &= c_j^0, \quad \phi = \phi_0 \\ y = l; \quad \frac{\partial c_j}{\partial y} &= \frac{\partial \phi}{\partial y} = 0 \end{aligned} \quad (9)$$

completely describe the electrode system. Here the boundary conditions represent one-half of an electrode exposed to bulk electrolyte (and counter-electrodes) on both sides, or so exposed on one side and sealed on the other.

The system of equations (7), (8) with boundary

conditions (9) can be solved for any desired form of the kinetic expression  $f(\eta, c_j)$  by computer implemented numerical techniques recently described by the authors<sup>10</sup>. The solution will give, in addition to the distribution of reaction and species concentration, the total current for any applied potential (or conversely, the potential at the electrode surface for any applied current density). Thus polarization curves are determined for any type kinetic expression.

### Electrode Kinetic Expressions

Many different forms may be used for the electrode kinetic (or local overpotential) expression,  $f(\eta, c_j)$ , some of which can be very complex indeed. This relationship, together with its parameters, is well established for relatively few reactions, but satisfactory approximations exist for a large number of others. The subject is discussed at length in such references as Vetter<sup>12</sup>. Certain types of expressions, developed either from theoretical models or from fitting of experimental data, have demonstrated considerable utility in practice.

Perhaps the most widely accepted form for a large class of reactions is the Volmer (or Volmer/Erdey-Gruz) expression

$$i^s = i_0 \left\{ \frac{c_r}{c_o} \exp \left[ \frac{\alpha nF \eta}{RT} \right] - \frac{c_p}{c_o} \exp \left[ \frac{(a-1)nF \eta}{RT} \right] \right\} \quad (10)$$

It applies to simple reversible reactions of the first

order and includes both forward and reverse reaction terms.

If the overpotential,  $\eta$ , is sufficiently high, the second (reverse) term in (10) becomes negligible and it reduces to the Tafel form:

$$i^s = i_o \frac{c_r}{c_o} \exp \left[ \frac{\alpha nF \eta}{RT} \right]. \quad (11)$$

This is frequently used as an approximation to the Volmer expression at high current densities (overpotentials).

At very low overpotentials the exponentials in (10) may be linearized resulting in the linear approximation

$$i^s = i_o \left\{ \left[ \frac{c_r}{c_o} - \frac{c_p}{c_p} \right] + \left[ \alpha \frac{c_r}{c_o} + (1-\alpha) \frac{c_p}{c_p} \right] \frac{nF \eta}{RT} \right\} \quad (12)$$

which may be used to replace the Volmer form at vanishing current densities. Of course, it is also possible to linearize (10) around any other value of the overpotential.

If concentration overpotential is neglected, or if concentrations are assumed uniform at bulk concentrations  $c_j^o$ , the Tafel type relationship assumes the more familiar form

$$i^s = i_o \exp \left[ \frac{\alpha nF \eta}{RT} \right], \quad (13)$$

and the linear approximation simplifies to

$$i^s = \frac{i_o nF \eta}{RT}, \quad (14)$$

which has the nature of an equivalent conductance  $\left( \frac{i_o nF}{RT} \right)$  relationship. If the transfer coefficient,  $\alpha$ , is further taken as  $\frac{1}{2}$ , the Volmer expression takes on the

the often used hyperbolic sine form,

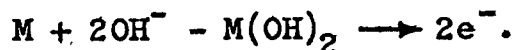
$$i^S = 2 i_0 \sinh \left[ \frac{nF \eta}{2 RT} \right]. \quad (15)$$

In this work the Volmer expression has been taken as the applicable electrode kinetic form, and the effects of variations in its parameters, and of replacement by Tafel and linear approximations, have been investigated.

### Electrode System

In order to investigate the influence of electrode kinetics on a flooded porous electrode it is necessary to examine a particular porous electrode system. For this purpose a slightly idealized metal-metal hydroxide anode operating in 5 N KOH has been selected. This example is typical in many respects of several practical electrodes (e.g., Cd - Cd(OH)<sub>2</sub>) while permitting arbitrary specification of parameters which might be subject to some question in a real system.

The anodic half cell reaction for the system is:



The electrolyte is binary, the significant species being K<sup>+</sup> and OH<sup>-</sup>. The system is thus described by:

$$z_+ = +1 ; z_- = -1$$

$$v_+ = 0 ; v_- = +2$$

$$c_+^0 = c_-^0 = 5 \times 10^{-3} \text{ gmol/cm}^3$$

$$n = -2.$$

The diffusion coefficient x Faraday products are taken as:

$$\left. \begin{array}{l} D_{+}F = 2 \text{ A cm}^2/\text{gmol} \\ D_{-}F = 4 \text{ A cm}^2/\text{gmol} \end{array} \right\} D_{\text{KOH}}F = 2.67 \text{ A cm}^2/\text{gmol}$$

giving a bulk solution specific resistance\*

$$\rho = 0.833 \Omega \text{ cm} .$$

The electrode reaction is taken to have Volmer kinetics with the parameters

$$i_0 = 10^{-2} \text{ A/cm}^2$$

$$\alpha = \frac{1}{2} .$$

The electrode matrix is symmetrically exposed to bulk solution and can be represented by the one dimensional model. It has an effective porosity of 0.5, a half thickness of 0.05 cm, a tortuosity factor of 2 and a specific surface  $10^3 \text{ cm}^{-1}$ .

This system will be designated as the "example electrode."

#### Polarization Curve for Example Electrode

The polarization curve calculated for the example electrode is shown in Figure 1. For comparison the curve for the equivalent plane (solid) electrode is included. The porous electrode has considerably lower polarization at all current densities than the plane and displays

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\* According to the Nernst-Einstein relation.

$$\frac{1}{\rho} = \frac{F^2}{RT} \sum_j^m z_j^2 D_j c_j^0$$

a roughly linear overpotential-current density behavior. The plane electrode polarization curve would be near linear against a logarithmic current density scale; thus over much of the range a Tafel slope (slope of  $\eta$  vs  $\log i$ ) could be specified. The porous electrode does not show this linear polarization vs log current density pattern. For it no meaningful Tafel slope can be defined.

For other electrode systems, and for other values of the electrode kinetic parameters, the porous electrode polarization curve may not be even approximately linear. However, the behavior will seldom be such as to follow a Tafel slope except over very narrow current density ranges or at very high polarizations.

#### Effect of Electrode Kinetic Parameters

With the example electrode polarization represented by a bold line as a base case, the effect of transfer coefficient,  $\alpha$ , in the Volmer expression (10) is illustrated in Figure 2. Here polarization curves for  $\alpha = 0.2$  and  $\alpha = 0.8$  are plotted with other parameters maintained as in the base example. As would be expected, low values of  $\alpha$  lead to greatly increased overpotentials, particularly at high current densities. Values of  $\alpha$  greater than 0.5 yield polarization curves somewhat lower than that for the example electrode.

The influence of exchange current density,  $i_0$ , is also shown in Figure 2. A reduction in  $i_0$  to  $10^{-3}$  A/cm<sup>2</sup>

from its example value of  $10^{-2}$  A/cm<sup>2</sup> gives a markedly increased polarization, and an increase to  $10^{-1}$  A/cm<sup>2</sup> yields considerably lower values. However, these changes in the polarization curves are relatively far less than would be expected for the same modifications of  $i_0$  at an equivalent plane electrode (where current at any given overpotential would be scaled according to  $i_0$ ). This damping in the influence of exchange current density is the result of the more effective utilization of the deeper portions of the porous electrode (more uniform current distribution) for cases of low  $i_0$  and the concentration of reaction near the electrode surface for high exchange current densities.

#### Effect of Modification of Electrode Kinetic Expression

If the form of the expression used to describe local electrode kinetics is modified, specifically to one of the limiting approximations described earlier, the predicted porous electrode polarization curve is significantly altered. This is illustrated in Figure 3. When the Volmer expression (10) is replaced by the Tafel representation (11) corresponding to it at high overpotentials, the predicted electrode polarization is considerably low over much of the current density range of interest. Although the Tafel form is an excellent approximation to the Volmer relationship for a plane electrode at overpotentials above about 20 mv, such is certainly not the case for a porous electrode. This discrepancy arises in the fact that even though the

polarization at the surface of the electrode is high enough to justify the Tafel approximation, the overpotential existing over much of the depth of the electrode may be too small to permit the disregarding of the reverse reaction term.

The use of the linear kinetic form corresponding to the Volmer expression at vanishing overpotential results in an electrode polarization curve which is a good approximation to the behavior of the example electrode at low current densities but which predicts excessively high polarizations at high current densities. This is shown by the "linear form (around  $\eta=0$ )" trace in Figure 3. The deviation here is less than for the equivalent plane electrode because the linear approximation will be better over much of the depth of the electrode than it is at the electrode face. The effect of linearization of the Volmer expression around some overpotential other than zero (here around  $\eta=25$  mv) is also presented in Figure 3.

The problems inherent in using limiting approximations to an overpotential approximation are apparent from the above examples. Since the reactions occurring in a porous electrode do so over a wide range of conditions dependent upon the depth of the reaction site in the electrode, no simplified kinetic form, intended to be used in the limit of high or low current densities, can be expected to apply throughout the electrode.



### Comparison with Results of Other Investigators

For comparison purposes the polarization curve of the example electrode was calculated by methods of several of the previous investigators cited above. These curves were universally lower than the predictions of the present work as shown in Figure 4. The differences are readily explained on the basis of assumptions involved in the analyses leading to the earlier results.

The curve predicted by the method of Ksenzhek and Stender<sup>1</sup> lies well below that found here for the example electrode. This deviation should be due entirely to the assumption of uniform electrolyte composition in these authors' work. In fact, if the present method is used with a kinetic expression in which concentration overpotential is specifically disregarded (15), a polarization behavior (dotted line in Figure 4) results which almost exactly matches the Ksenzhek and Stender prediction\*.

The polarization according to the technique of Euler and Nonnenmacher<sup>3</sup> agrees quite well with the present investigation. The assumptions of uniform electrolyte concentration, tending to give low overpotentials, and of a linear kinetic expression, yielding high overpotentials, here have largely offset each other. The

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\* The residual variation arises in the nonuniform conductivity that exists in the pores because of the nonuniform concentrations present and in Ksenzhek and Stender's use of an infinitely thick electrode.

work of Newman and Tobias<sup>4</sup> does not possess this compensating feature, both the uniform concentration and Tafel kinetic assumptions tending to give low polarization predictions. Therefore this method yields consistently low overpotential values.

The overpotential-current density behavior calculated according to Ksenzhek<sup>5</sup> shows behavior characteristic of the use of Tafel kinetics and is in good agreement with the curve that would be given by the present treatment using such an electrode kinetic expression. This is true in spite of the fact that the example electrode does not have excess inert electrolyte as assumed by Ksenzhek; the relatively concentrated electrolyte solution of the case considered is sufficient to make Ksenzhek's hypothesis of uniform potential in the pores not far in error.

### Conclusions

Examination of the influence of electrode kinetic expressions in calculation of the polarization curves for flooded porous electrodes leads to several general observations concerning these effects.

The deviation of the overpotential-current density relationship for a porous electrode from that for an equivalent plane electrode is not only in magnitude but also in form. The linearity of the overpotential-log current density plots found for solid electrodes cannot be expected in most cases where porous electrodes are involved.

Use of asymptotic approximations to electrode kinetic expressions must be undertaken with caution. If a reaction is properly characterized by a Volmer type kinetic expression, use of a Tafel or linear limiting form will often result in quite spurious predictions of polarization behavior. Further, assumption of uniformity of electrolyte concentration in a porous electrode at steady state can yield significantly low calculated overpotentials. The sensitivity of computed results to the nature and parameters of the local overpotential expression demonstrates the need for better basic kinetic data.

This study indicates the necessity for individual examination of each electrode for which overpotential-current density curves are to be calculated, and for the avoidance of simplified rules for deriving polarization of a porous electrode in terms of that of a corresponding flat plate.

#### Acknowledgement

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## NOTATION

- $a$  = Specific surface of porous electrode ( $\text{cm}^{-1}$ ).  
 $c_j$  = Concentration of species  $j$  ( $\text{gmol}/\text{cm}^3$ ).  
 $c_j^0$  = Concentration of species  $j$  in bulk electrolyte ( $\text{gmol}/\text{cm}^3$ ).  
 $D_j$  = Diffusion coefficient of species  $j$  ( $\text{cm}^2/\text{sec}$ ).  
 $e^-$  = Symbol for electron.  
 $F$  = Faraday's constant (96 500 C/equiv.).  
 $i$  = Current density in electrolyte ( $\text{A}/\text{cm}^2$ ).  
 $i_0$  = Exchange current density for electrode reaction ( $\text{A}/\text{cm}^2$ ).  
 $i^s$  = Transfer current density ( $\text{A}/\text{cm}^2$ ).  
 $l$  = Thickness (or half thickness) of porous electrode model (cm).  
 $m$  = Number of species present in electrolyte.  
 $M_j$  = Symbol for species  $j$ .  
 $N_j$  = Flux of species  $j$  in electrolyte ( $\text{gmol}/\text{cm}^2\text{sec}$ ).  
 $n$  = Number of Faradays of charge transferred per g mol of reaction.  
 $R$  = Gas constant.  
 $S_j$  = Source term for species  $j$  ( $\text{gmol}/\text{cm}^3\text{sec}$ ).  
 $T$  = Absolute temperature ( $^{\circ}\text{K}$ ).  
 $u_j$  = Mobility of species  $j$  (cm/sec dyne).  
 $y$  = Distance into porous electrode (cm).  
 $z_j$  = Charge number of species  $j$ .

## Greek Letters

$\alpha$  = Transfer coefficient for electrode reaction.

$\epsilon$  = Electronic charge ( $1.60 \times 10^{-19}$  coul).

$\eta$  = Electrode overpotential (V).

$\nu_j$  = Stoichiometric coefficient of species j.

$\phi$  = Potential in electrolyte (reference matrix) (V).

## Subscripts

j = Species in electrolyte.

r = Reactant species.

p = Product species.

Figure 1. Polarization Curve for Example Porous Electrode Compared with Polarization for Equivalent Plane Electrode.

Figure 2. Effect of Parameters  $\alpha$  and  $i_0$  in Volmer Kinetic Expression upon Polarization Curve for Example Porous Electrode.

Figure 3. Effect of the Form of Electrode Kinetic Expression upon Polarization Curve for Example Porous Electrode.

Figure 4. Polarization Curve for Example Porous Electrode Compared to Curves Predicted for this Electrode by Methods of Some Other Investigators.

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